

## O 40: Metal substrates: Adsorption of organic / bio molecules V

Time: Wednesday 11:15–13:00

Location: PHY C213

O 40.1 Wed 11:15 PHY C213

**Bonding and metalation of 2H-TTP on the Cu(111) surface—a multitechnique study** — ●KATHARINA DILLER<sup>1</sup>, FLORIAN KLAPPENBERGER<sup>1</sup>, KLAUS HERMANN<sup>2</sup>, and JOHANNES V. BARTH<sup>1</sup> — <sup>1</sup>Physik Department, E20, Technische Universität München, James-Frank-Str. 1, 85748 Garching, Germany — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Germany

We report on the interaction of free base tetraphenylporphyrin (2H-TTP) molecules with the Cu(111) surface studied with a multitechnique approach combining x-ray photoelectron spectroscopy (XPS) and near-edge x-ray absorption fine structure spectroscopy (NEXAFS) measurements with density functional theory (DFT) calculations. After the adsorption of 2H-TTP on Cu(111) at room temperature the spectroscopic signatures (XPS and NEXAFS) depend on the molecular coverage. Near to a saturated monolayer NEXAFS indicates a strongly deformed macrocycle and electron transfer into the LUMO. XPS reveals that the adsorbate is a free base porphyrin. After annealing both XPS and NEXAFS data show the signature of a metalloporphyrin with a relaxed macrocycle. DFT calculations corroborate the peak assignment used for the analysis of the XPS and the NEXAFS data and provide information on the electronic structure of isolated 2H-TTP and Cu-TTP molecules.

O 40.2 Wed 11:30 PHY C213

**Metalation of tetrapyrroldiporphyrin with Cu atoms on Au(111): aspects of structure and reactivity** — ●JIE XIAO<sup>1</sup>, MARTIN SCHMID<sup>1</sup>, MIN CHEN<sup>1</sup>, ZILIANG SHI<sup>2</sup>, NIAN LIN<sup>2</sup>, TATYANA SHUBINA<sup>3</sup>, TIMOTHY CLARK<sup>3</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, and MICHAEL GOTTFRIED<sup>1</sup> — <sup>1</sup>Universität Erlangen-Nürnberg, Lehrstuhl für Physikalische Chemie II, Erlangen, Germany — <sup>2</sup>Hong Kong University of Science and Technology, Hong Kong, China — <sup>3</sup>Universität Erlangen-Nürnberg, Computer-Chemie-Centrum, Erlangen, Germany

The reaction between a submonolayer of tetrapyrroldiporphyrin (2HT-PyP) on Au(111) and co-deposited Cu atoms was studied by temperature-dependent X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The Cu atoms undergo two simultaneous reactions with 2HTPyP: (1) Metalation of the porphyrin core and (2) coordination by pairs of pyridyl groups of adjacent 2HT-PyP molecules. At 300 K, the metalation reaction (1) leads mainly to a metastable initial complex, Cu-2HTPyP, in which Cu remains in the zero oxidation state. At elevated temperatures, Cu is oxidized by the porphyrin ligand, forming copper(II) tetrapyrroldiporphyrin (CuT-PyP). Further details of the complex reaction mechanism are revealed by DFT calculations. The coordination reaction (2) leads to the formation of a 2D metal-organic coordination network, which gradually degrades at higher temperatures due to bulk diffusion of Cu, resulting in close-packed molecular monolayer stabilized by intermolecular hydrogen bonds. Supported by the Deutsche Forschungsgemeinschaft through SFB 583 and by the Alexander von Humboldt Foundation.

O 40.3 Wed 11:45 PHY C213

**Adsorption behaviour of CoPc and CoTMPP on Cu(110) and Cu(110)-(2x1)O** — ●DANIEL QUETESCHNER, MARIELLA DENK, MICHAEL HOHAGE, and PETER ZEPPENFELD — Institute of Experimental Physics, Johannes Kepler University Linz, A-4040 Linz, Austria

The geometric arrangement of cobalt-phthalocyanine (CoPc) and cobalt-tetra(4-methoxyphenyl)porphyrin (CoTMPP) on the Cu(110) and Cu(110)-(2x1)O surface was investigated for coverages up to 1 ML by a combination of reflectance difference spectroscopy (RDS), low energy electron diffraction (LEED), and scanning tunneling microscopy (STM).

On Cu(110) both molecules adsorb at room temperature in a 2D-gas. Upon cooling to  $T = 14$  K CoTMPP condenses into a well-ordered structure while for CoPc the gas phase is maintained.

On the oxygen reconstructed Cu surface, however, both CoPc and CoTMPP form well-ordered structures even at room temperature. Continuing the growth up to the saturated ML, the CoTMPP layer undergoes two coverage driven transitions between distinct superstructures.

O 40.4 Wed 12:00 PHY C213

**DFT Calculations on the Electronic Interaction of Iron-Phthalocyanine with the Ag(111)-Surface** — ●MARTIN CALLSEN<sup>1,2</sup> and ECKHARD PEHLKE<sup>2</sup> — <sup>1</sup>Peter Grünberg Institut & Institute for Advanced Simulation, Forschungszentrum Jülich and JARA, 52425 Jülich, Germany — <sup>2</sup>Institut für Theoretische Physik und Astrophysik, Christian-Albrechts-Universität zu Kiel, 24098 Kiel

Organic molecules adsorbed on metal-surfaces play an important role for the functionalization of surfaces or as candidates for electronic devices in the emerging field of nano-electronics. As such metal-phthalocyanines (MPc) are an intensely studied model-system, both experimentally in STM/STS-measurements and theoretically by density functional theory (DFT) calculations. For the latter it is known that there are still problems concerning the correct treatment of dispersion interactions and the exact description of excitation spectra of organic molecules. For this reason a detailed comparison with experiments will be helpful. Iron-phthalocyanine (FePc) adsorbed on the Ag(111)-surface has been investigated by spin-polarized total energy calculations employing DFT as implemented in the VASP-code. The PAW-pseudopotential-method has been applied and as approximation for the xc-functional GGA-PBE has been used. To account for dispersion interactions the empirical  $C_6/R^6$ -ansatz [1] has been applied.

[1] S. Grimme, J. Comput. Chem. **27**, 1787 (2006)

O 40.5 Wed 12:15 PHY C213

**Stabilization by rotational entropy - A general attribute of 'large' adsorbates?** — ●THOMAS WALDMANN<sup>1</sup>, HARRY E. HOSTER<sup>1,2</sup>, and R. JÜRGEN BEHM<sup>1</sup> — <sup>1</sup>Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm, Germany — <sup>2</sup>Current address: Technische Universität München, Centre for Electromobility, 50 Nanyang Drive, Singapore 637553

Large molecules have in general considerable moments of inertia. At sufficiently high temperatures and not too high coverages this can lead to a stabilization of the adlayer by rotational entropy, as shown, e. g., in a recent thermal desorption (TPD) study [1] of the bisterpyridine derivative 2,4'-BTP on graphite (HOPG). In this presentation we used 2,4'-BTP on Ag(111) as a model system, where this behavior was directly observed by scanning tunneling microscopy (STM) at 300 K. Domains of freely rotating 2,4'-BTP molecules are in a dynamic equilibrium with static disordered 2D islands (2,4'-BTP)<sub>n</sub> ( $n > 1$ ) and individual molecules ( $n=1$ ) stabilized by lateral (N...H) and vertical (N...Ag) interactions [2]. Evaluating a large number of molecules in STM images, we determined the mean energy difference between the rotating and the non-rotating adsorbates in the 2D islands. The stabilization by rotational entropy is compared with that of other typical small ( $O_2$ ,  $N_2$ , acetylene) and large (benzene, PTCDA, 3,3'-BTP, HB-DC, MPc) adsorbates at 300 K.

[1] M. Roos et al., PCCP **12**, 812 (2010).[2] T. Waldmann et al., ChemPhysChem **11**, 1513 (2010).

O 40.6 Wed 12:30 PHY C213

**Interplay of acceptor and donor species in charge-transfer complexes** — ●TOBIAS R. UMBACH<sup>1</sup>, ISABEL FERNÁNDEZ-TORRENTE<sup>1</sup>, JANINA LADENTHIN<sup>1</sup>, MICHAEL KLEINERT<sup>1</sup>, ROBERT DROST<sup>1</sup>, RICCARDO RURALI<sup>2</sup>, JOSE I. PASCUAL<sup>1</sup>, and KATHARINA J. FRANKE<sup>1</sup> — <sup>1</sup>Institut für Experimentalphysik, Freie Universität Berlin, Arnimallee 14, 14195 Berlin, Germany — <sup>2</sup>Institut de Ciència de Materials de Barcelona (ICMAB), Consejo Superior de Investigaciones Científicas (CSIC), Campus de Bellaterra, 08193 Bellaterra (Barcelona), Spain

The redistribution of charge between donor and acceptor species plays a key role for tuning the electronic functionality of organic compounds. By low temperature scanning tunneling microscopy and spectroscopy (LT-STM, LT-STS) we investigate molecular layers of the donor acceptor complexes Na-TCNQ, Na-TNAP, TTF-TNAP and TTF-TCNQ on a Au(111) surface. Due to the presence of the metallic surface the amount of charge transfer (CT) and its localization can differ from the bulk system. Both TTF-TCNQ and Na-TCNQ exhibit a CT of one electron, demonstrated by the presence of the Kondo resonance. In the case of Na-TCNQ the electron is localized at the Na-CN bond, whereas for TTF-TCNQ it lies in the conjugated lowest unoccupied molecular orbital. By changing the molecular acceptor the CT can be varied. TCNQ offers a lower electron affinity and higher symmetry

compared to TNAP. In contrast to the first two systems, Na-TNAP as well as TTF-TNAP show no Kondo resonance, evidencing an even or non-integer CT.

O 40.7 Wed 12:45 PHY C213

**STM/STS-Study of Spiro-DPO molecules on Au(111) up to two monolayers coverage** — •MICHAEL WAELSCH<sup>1</sup>, BENJAMIN HERATH<sup>1</sup>, TOBAT P. SARAGI<sup>2</sup>, JOSEF SALBECK<sup>2</sup>, and RENÉ MATZDORF<sup>1</sup> — <sup>1</sup>AG Experimentalphysik 2, Oberflächenphysik — <sup>2</sup>AG Makromolekulare Chemie und Molekulare Materialien, Univer-

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In the Spiro-DPO-molecule an arylamine group (acceptor) is linked to an oxadiazole group (donor) via a spiro-C-atom. Coverages of 1/10...2 ML of the organic semiconductor Spiro-DPO have been investigated with STM/STS at 4.7 K. Large islands of homochiral molecules were observed, whose internal double-row structure is oriented in an  $\pm 10^\circ$  angle relative to the Au-crystal axes. Spatially resolved tunneling spectra show different LUMO-energies of the donor/acceptor groups of one molecule.